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Synthesis of Functionalized Fluorescent Indenes from Electron-Rich α-Aryl Ketonitriles

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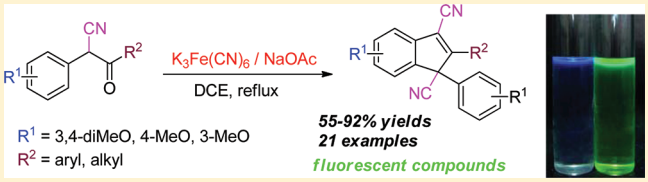
Supporting Information

ABSTRACT: A series of functionalized indenes bearing 1,3-dicyano groups were synthesized from electron-rich α-aryl ketonitriles in the presence of $K_3Fe(CN)_6$ and NaOAc, possibly through tandem process involving dimerization, heterolytic cleavage of carbon−carbon bond, intermolecular coupling, and the subsequent intramolecular cyclization. The 2-arylindene compounds obtained possess good fluorescent properties.



INTRODUCTION

Indenes show a wide range of biological activities[1] and possess great interest as functional materials as well as precursors for catalysts of olefin polymerization.[2] Consequently, recent years have witnessed a number of reports on the construction of the indene ring system. The most effective approaches for the synthesis of indenes include the reduction or dehydration of indanones,[3] acid-catalyzed cyclodehydration of the phenyl-substituted allylic alcohols,[4] the ring expansion of certain substituted cyclopropenes,[5] and Lewis-acid catalyzed Friedel−Crafts cyclization of aryl allenes.[6] In addition to these classical methods, transition metal[7] catalyzed carboannulations of alkynes have also been proven to be useful tools for the access to indene rings. Each of these methods has its own merit in the preparation of the corresponding indene compound with specific substitution pattern. Herein, we described a novel method that can afford a variety of highly functionalized fluorescent indenes, which are undoubtedly difficult to achieve by the existing approaches.

It has been well documented that the α-aryl ketonitriles can undergo oxidative coupling reactions at benzylic position to afford the diastereomeric homodimers in the presence of various oxidants such as $K_3Fe(CN)_6$, $KMnO_4$, Ag_2O and PbO_2 (Figure 1, path a).[8] Alternatively, the electron-rich α-aryl ketonitriles can also be converted into benzo[*b*]furan compounds via intramolecular oxidative C−O bond formation mediated by $FeCl_3$, which acts as a single electron-oxidant (Figure 1, path b).[9] However, to the best of our knowledge, the formation of indene compound directly from α-aryl ketonitriles has not been reported before.

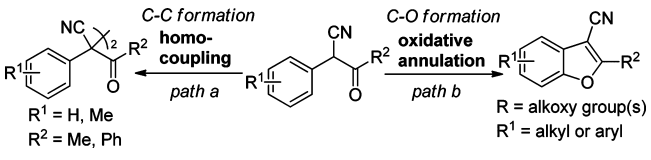


Figure 1. The existing oxidative reactions of α-aryl ketonitriles.

RESULTS AND DISCUSSION

Initially, we treated the electron-rich α,β-diaryl ketonitrile **1a** with $K_3Fe(CN)_6$, anticipating that the reaction would adopt the "path a" depicted in Figure 1 to give the corresponding homocoupled product. Unexpectedly, the reaction of **1a** with $K_3Fe(CN)_6$ in the presence of NaOAc in acetone under reflux for 12 h was found to give the fluorescent compound **2a**. The result of X-ray crystal analysis clearly indicated that it is a novel highly substituted indene compound (see the Supporting Information for details).

Encouraged by this finding, **1a** was used as a model substrate to investigate the different parameters in order to optimize the reaction conditions (Scheme 1). Screening of a series of other solvents, including THF, 1,4-dioxane, DCE, EtOAc, MeCN, EtOH, and DMF (Table 1, entries 2−8), showed that the reaction in DCE at reflux afforded the best yield in 88% (Table 1, entry 4). Control experiment implied that the reaction turned out to be sluggish if it was operated at room temperature (Table 1, entry 9).

Furthermore, the base was found to be indispensable for the conversion of **1a** to **2a** since no reaction occurred in the absence of NaOAc (Table 1, entry 10). An examination of the other bases revealed that Na_2CO_3 also provided a good yield of **2a**, while the use of pyridine or triethylamine afforded the product in much lower yield in each case. Finally, for comparison we also carried out the reaction using other iron(III) compounds. The results showed that no reaction

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Scheme 1. Proposed Reaction Pathway

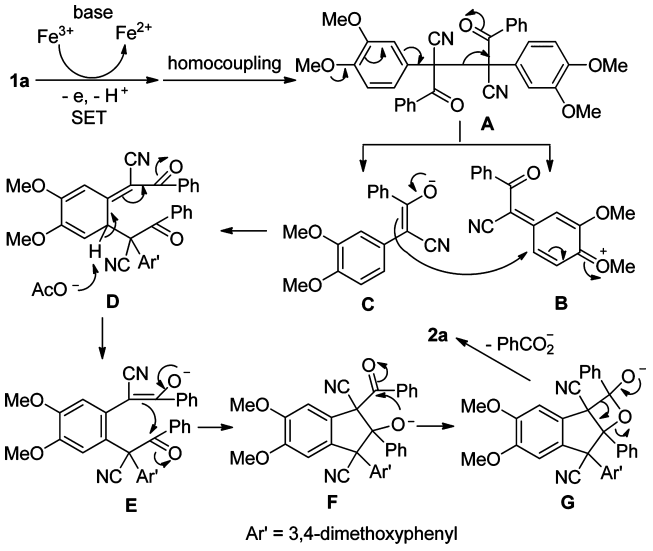
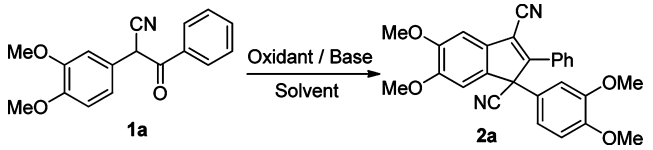


Table 1. Reaction Conditions Optimization for $K_3Fe(CN)_6$-Mediated Synthesis of Indenes



entry[a]	solvent	oxidant	base	yield (%)[b]
1	acetone	$K_3Fe(CN)_6$	NaOAc	38
2	THF	$K_3Fe(CN)_6$	NaOAc	30
3	dioxane	$K_3Fe(CN)_6$	NaOAc	59
4	DCE	$K_3Fe(CN)_6$	NaOAc	88
5	EtOAc	$K_3Fe(CN)_6$	NaOAc	56
6	CH_3CN	$K_3Fe(CN)_6$	NaOAc	41
7	EtOH	$K_3Fe(CN)_6$	NaOAc	15[c,e]
8	DMF	$K_3Fe(CN)_6$	NaOAc	10[c]
9	DCE	$K_3Fe(CN)_6$	NaOAc	10[d,e]
10	DCE	$K_3Fe(CN)_6$		NR
11	DCE	$K_3Fe(CN)_6$	Na_2CO_3	82
12	DCE	$K_3Fe(CN)_6$	TEA	70
13	DCE	$K_3Fe(CN)_6$	pyridine	50
14	DCE	$Fe(NO_3)_3·9H_2O$	NaOAc	NR[e]
15	DCE	$Fe(acac)_3$	NaOAc	NR[e]

[a]Conditions: **1a** (0.4 mmol), oxidant (3 equiv), and base (2 equiv) reflux in solvent (4 mL) for 12 h. [b]Isolated yields. [c]Retarded by unidentified byproducts. [d]Carried out at rt, based on 30% conversion of dimerized intermediate. [e]The reaction time was prolonged to 24 h.

occurred when either $Fe(acac)_3$ or hydrated $Fe(NO_3)_3$ was applied.

Under the optimal reaction conditions, a series of substrates bearing various substituents were employed to investigate the scope of the method, and the results are summarized in Table 2. The reaction was found to tolerate a range of different substituents on the β-phenyl ring in the substrates. When the diaryl ketonitriles **1c–e** (not shown) were substituted with methoxy groups on the β-phenyl ring, they were converted into the corresponding indene **2c–e** in good to excellent 92, 90, and 80% yields, respectively. The substrates bearing halogen(s) substituted at *para*, *meta*, or *ortho* position of the β-phenyl ring also proceed successfully to afford the desired products **2f–j** in moderate to good yields. Furthermore, this method works equally well for the substrates bearing the strong electron-withdrawing trifluoromethyl group.

The substrate scope can be expanded with the β-phenyl ring being changed with the thienyl, furyl, or pyridinyl rings. Notably, when a vinyl group was inserted between the carbonyl group and the aryl group in substrate **1a** as a conjugation bridge, the related ketonitrile **1p** (not shown) was successfully converted to indene **2p** under the described conditions. Intriguingly, when the β-aryl ring in the substrate was changed to alkyl groups, the reactions also occurred to afford indene products **2r** and **2s** in good yields of 68 and 78%, respectively. Next, we turned to replace the α-phenyl ring with other substituents. Substrates with only one methoxy group at either *para* or *meta* position of the α-phenyl ring were also applicable to give the corresponding indenes **2s** and **2t**, however in relatively much lower yields. In addition, when the α-phenyl ring was replaced with a methoxy substituted naphthyl ring, the corresponding indene **2u** can be obtained in a good 75% yield.

Furthermore, we found that methoxy group(s) on the α-phenyl ring of the substrate is crucial for the reaction to occur. The reaction failed for the α-phenylacetoacetonitrile (**1v**) and α-phenylbenzoylacetonitrile (**1w**), in which the α-phenyl ring bears no methoxy group. In both of these two cases, the reactions adopt "path a" depicted in Figure 1 to give the homodimerized products.

A possible mechanistic pathway is proposed for this heterocoupling/cyclization process (Scheme 1). On the basis of the experimental fact that substrates without any methoxy substituents on the α-phenyl ring will undergo homocoupling at the benzylic position to give a dimer under the same conditions, we postulated that the first step in the mechanistic sequence might be the formation of the homodimer **A**, from the benzylic radical intermediate (not shown) generated by the single electron transfer process mediated by $K_3Fe(CN)_6$ in the presence of base. Next, the electron-donating methoxy group in the α-phenyl ring and the electron-withdrawing cyano and carbonyl groups in intermediate **A** might exert the "push–pull" effect, which leads to the heterolytic cleavage of the carbon–carbon bond under thermal conditions to give the oxonium intermediate **B** and enolate **C**. Subsequently, the conjugate addition of enolate **C** to intermediate **B** affords the adduct **D**. Further deprotonation from **D** realizes the rearomatization of the phenyl ring and the formation of enolate **E**. The subsequent intramolecular cyclization of **E** gives intermeidate **F**, which undergoes further cyclization to form a four-membered ring intermediate **G**. Finally, after the removal of one molecule of benzoate anion, the title indene compound **2a** can be achieved. In all of the above reactions, the fragmented aryl carboxylic acid (after acidic workup) can be detected by TLC comparison.

In order to test the possibility of the carbon–carbon bond cleavage process described above, we came to subject the homodimers **1a′**, **1f′**, and **1q′** to the identical reflux conditions (Scheme 2). As expected, the corresponding indene products can be formed in good yields. However, the homodimers of **1v** and **1w**, without methoxy group on the α-phenyl ring, provided no indene product at reflux in DCE even for 24 h, which proved that the methoxy group substituted on the α-phenyl ring played a vital role in the process.

Furthermore, a preliminary survey of the optical properties of this series of compounds was carried out. The photophysical properties of some representative indenes are outlined in

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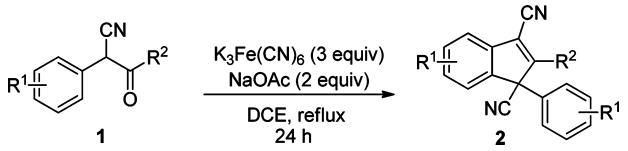
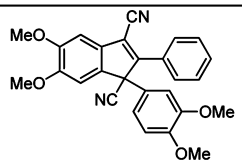
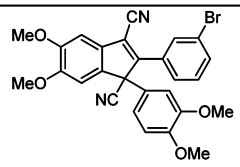
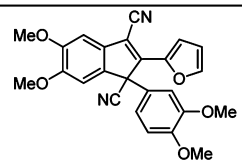
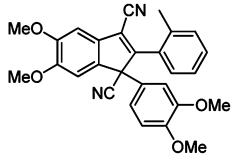
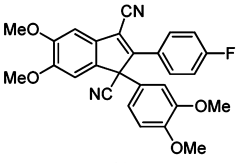
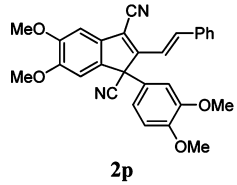
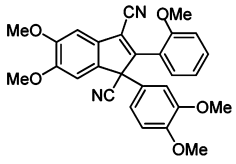
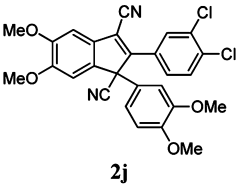
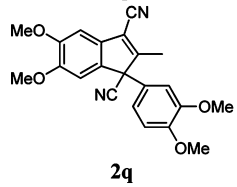
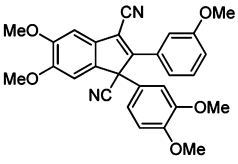
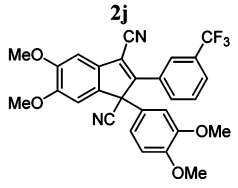
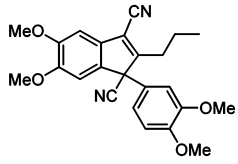
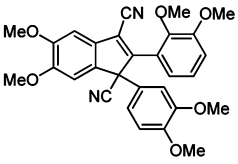
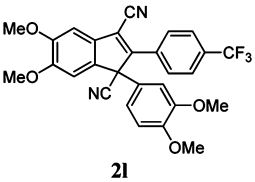
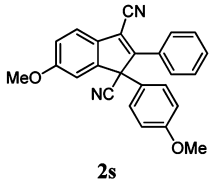
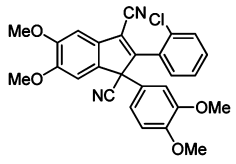
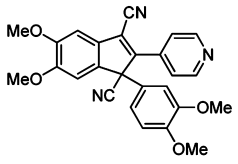
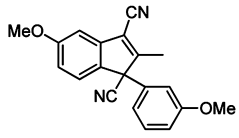
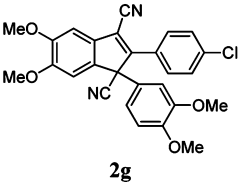
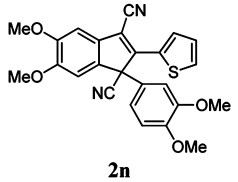
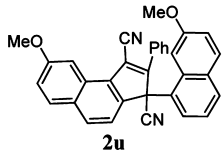
Table 2. Synthesis of Functionalized Indenes from Electron-Rich α-Aryl Ketonitriles[a]



entry	indenes **2**	yield (%)[b]	entry	indenes **2**	yield (%)[b]	entry	indenes **2**	yield (%)[b]
1	 **2a**	88	8	 **2h**	91	15	 **2o**	71
2	 **2b**	69	9	 **2i**	67	16	 **2p**	65
3	 **2c**	92	10	 **2j**	82	17	 **2q**	68
4	 **2d**	90	11	 **2k**	84	18	 **2r**	78
5	 **2e**	80	12	 **2l**	81	19	 **2s**	55
6	 **2f**	69	13	 **2m**	82	20	 **2t**	58
7	 **2g**	86	14	 **2n**	81	21	 **2u**	75

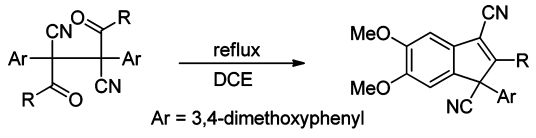
[a]All the reactions were carried out with **1a** (0.4 mmol), $K_3Fe(CN)_6$ (3 equiv), and Na_2CO_3 (2 equiv) reflux in DCE (4 mL) for 12 h. [b]Isolated yields.

Figure 2 and Table 3 (for the optical data of all the indenes **2**, see the Supporting Information).

All target compounds listed in Table 2 exhibit fluorescence property except for those where R^2 is an alkyl group (**2q**, **2r**, and **2t**). This indicates that π conjugation exists between the unsaturated R^2 substituent and the main π skeleton of the indene, and it is this conjugation that significantly lowers the HOMO−LUMO (highest occupied molecular orbital−lowest unoccupied molecular orbital) gap and consequently pushes the absorption and emission wavelengths, λ_{abs} and λ_{em}, respectively, from the UV region to the visible region.[10] The planar skeleton of the indenes with a conjugated π-system enables them to possess relatively larger Stokes shifts of around 84−130 nm, with quantum yield ranging from 0.46 to 0.72.[11]

dx.doi.org/10.1021/jo300367q | J. Org. Chem. 2012, 77, 3997−4004

Scheme 2. Evidence of the Carbon−Carbon Bond Cleavage under the Thermal Conditions



Ar = 3,4-dimethoxyphenyl

1a' (R = Ph)	70%	**2a** (R = Ph)
1h' (R = 3-Br-Ph)	90%	**2h** (R = 3-Br-Ph)
1q' (R =Me)	80%	**2q** (R = Me)

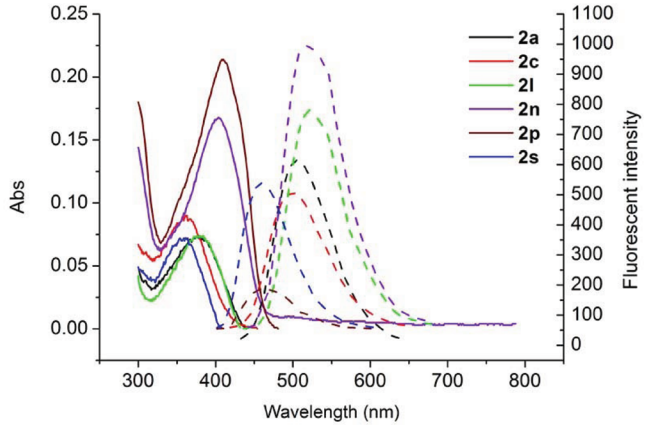


Figure 2. Absorption spectra (solid line) and fluorescence spectra (dashed line) in CH_2Cl_2.

Table 3. Optical Data of Representative Indenes

indenes	λ_{abs} (nm)[a]	ε_{max} (M^{-1} cm^{-1})[b]	λ_{em} (nm)[a]	Stokes shift (cm^{-1})	φ[c]
2a	375	7300	506	91743	0.68
2c	363	9000	498	84746	0.55
2l	390	8100	523	80000	0.55
2n	404	16800	519	95238	0.52
2p	408	21400	518	101010	0.48
2s	361	7200	461	119048	0.46

[a]Wavelengths of maximum absorbance (λ_{abs}) or emission intensity (λ_{em}). [b]Extinction coefficient. [c]Quantum yield determined by using Rhodamine B as a standard (φ = 0.71).

Substituent effect on the energy gap of the HOMO and LUMO affect the fluorescent properties of the indenes dramatically. It is obvious that the introduction of an electron-donating methoxy group to the α-phenyl ring, which is known to increase the occupied molecular orbitals, leads to a red-shift maximum comparing **2a** with **2s** as well as the increase of quantum yield from 0.46 to 0.68. Substituents of the β ring changing from methoxyl (**2c**) to trifluoromethyl (**2l**) and thienyl group (**2n**) cause bathochromic emission wavelength shifts from 498 to 523 and 519 nm. Relative to **2a**, the hypsochromic behavior in **2c** is probably caused by reduced π conjugation due to the steric effect of the bulky methoxyl group on the β-phenyl ring. The red shift of **2p** can be rationalized by the more extended π system as a result of an extra —CH═CH— group. We suggested that the increase of both emission wavelength and Stokes shift of **2l** might be attributed to the "push−pull" effect of the π-electron mode, in which the methoxy groups act as electron donor and the electron-withdrawing group (trifluoromethyl) of the indene acts as electron acceptor.[12] As to the bathochromic shift of **2n**, we hypothesized that it might be ascribed to the π^6_5 system of thienyl ring, which is more electron-rich than the π^6_6 system of phenyl ring,[13] and therefore decreases the energy gap of the HOMO and LUMO.[14]

CONCLUSION

In conclusion, we have demonstrated a novel method to synthesize functionalized indenes bearing 1,3-dicyano groups, which features inexpensive reagents and mild reaction conditions. Mechanistic study suggests that the reaction involves an interesting tandem process involving dimerization, heterolytic cleavage of carbon−carbon bond, intermolecular coupling, and the subsequent intramolecuar cyclization.

EXPERIMENTAL SECTION

General Information. All reactions were carried out at room temperature without precaution of air and stirred magnetically. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer at 25 °C. Chemical shift values are given in ppm and referred as the internal standard to TMS: 0.00 ppm. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; m, multiplet, and dd, doublet of doublets. The coupling constants, J, are reported in Hertz (Hz). High resolution mass spectrometry (HRMS) was obtained on a Q-TOF microspectrometer. Melting points were determined with MicroMelting point apparatus without corrections. Organic solutions were concentrated by rotary evaporation below 40 °C in a vacuum. TLC plates were visualized by exposure to ultraviolet light. Reagents and solvents were purchased as reagent grade and were used without further purification. All reactions were performed in standard glassware, heated at 110 °C for 3 h before use. Flash column chromatography was performed over silica gel 100−200 m, and the eluent was a mixture of ethyl acetate (EA) and petroleum ether (PE). All the UV/vis spectra were performed on a spectrofluorimeter, and fluorescent measurement was carried out on a fluorescent spectrofluorimeter with a concentration of 10 μM in CH_2Cl_2. The quantum yields were measured using Rhodamine B as a standard (φ = 0.71).[15−17]

Ketonitriles **1a−1u** were prepared according to the literature.[9,18]

General Procedure for the Synthesis of Indenes (2a−2u). To a solution of α-aryl ketonitriles **1** (0.4 mmol) in 1,2-dichloroethane (4 mL) were added potassium ferricyanide (0.395 g, 1.2 mmol) and sodium acetate (0.066 g, 0.8 mmol) with efficient stirring at room temperature. The mixture was then heated at reflux, and the process of the reaction was monitored by TLC analysis. After the completion of the reaction, the reaction mixture was filtered and washed with 1,2-dichloroethane (15 mL × 3). The filtrate was concentrated in a vacuum to remove the solvent. The residue was purified by silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products **2**.

2-(3,4-Dimethoxyphenyl)-3-oxo-3-(*o*-tolyl)propanenitrile (1b). 1b was purified by silica gel chromatography (EA/PE = 15/85): yield 2.235 g, 67%, isomers (enol/ketone ratio 5:1) are reported together, white solid; ^1H NMR (400 MHz, $CDCl_3$) major isomer (enol) δ 7.37 (d, J = 7.0 Hz, 1H), 7.32 (d, J = 7.0 Hz, 1H), 7.25−7.17 (m, 5H, peaks of two isomers overlapped), 6.88 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H), 3.3.86 (s, 3H), 2.37 (s, 3H), minor isomer (ketone) δ 7.25−7.17 (m, 5H, peaks of two isomers overlapped), 6.64 (s, 2H), 6.24 (s, 1H), 3.76 (s, 3H), 3.39 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) major isomer (enol) δ 164.8, 149.3, 148.9, 136.4, 134.3, 130.8, 130.6, 129.0, 126.1, 123.8, 120.9, 119.1, 111.5, 111.0, 91.9, 56.0, 56.0, 19.4 (the ^{13}C NMR data of the minor isomer was not collected because of the low concentration); HRMS (ESI) m/z calcd for $C_{18}H_{18}NO_3^+$ $[M + H]^+$ 296.1281, found 296.1283.

2-(3,4-Dimethoxyphenyl)-3-(3-methoxyphenyl)-3-oxopropanenitrile (1d). 1d was purified by silica gel chromatography (EA/PE = 20/80): yield 2.710 g, 77%, white solid, mp 111−113 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.11 (dd, J = 8.0, 2.0 Hz, 1H), 6.97 (dd, J =

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8.0, 2.0 Hz, 1H), 6.90 (d, J = 2.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 5.58 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 160.0, 149.9, 149.7, 135.0, 129.9, 122.6, 121.6, 121.1, 120.8, 116.8, 113.6, 111.8, 110.8, 56.1, 55.9, 55.5, 46.4; HRMS (ESI) m/z calcd for $C_{18}H_{18}NO_4^+$ $[M + H]^+$ 312.1230, found 312.1231.

(*E*)-3-(2,3-Dimethoxyphenyl)-2-(3,4-dimethoxyphenyl)-3-hydroxyacrylonitrile (1e). **1e** was purified by silica gel chromatography (EA/PE = 20/80): yield 2.735 g, 71%, white solid, mp 121−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.41 (d, J = 7.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H), 6.95−6.82 (m, 2H), 3.96−3.84 (m, 9H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 152.5, 148.7, 148.5, 145.7, 129.0, 124.8, 124.7, 122.2, 121.2, 120.2, 114.5, 111.6, 111.1, 92.0, 61.7, 56.0, 55.9, 55.7; HRMS (ESI) m/z calcd for $C_{19}H_{20}NO_5^+$ $[M + H]^+$ 342.1336, found 342.1338.

3-(2-Chlorophenyl)-2-(3,4-dimethoxyphenyl)-3-oxopropanenitrile (1f). **1f** was purified by silica gel chromatography (EA/PE = 20/80): yield 2.845 g, 68%, isomers (enol/ketone ratio 5:1) are reported together, white solid; ^{1}H NMR (400 MHz, $CDCl_3$), major isomer (enol), δ 7.57 (dd, J = 7.5, 2.0 Hz, 1H), 7.50 (dd, J = 7.5, 1.0 Hz, 1H), 7.44 (t, J = 7.5, 2.0 Hz, 1H), 7.41−7.35 (m, 1H), 7.30−7.28 (m, 1H), 7.24 (d, J = 2.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.74 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.81 (s, 1H), 3.56 (s, 1H), minor isomer (ketone), 7.24 (d, J = 2.0 Hz, 2H), 7.21−7.18 (m, 2H), 6.68−6.64 (m, 2H), 6.50 (s, 1H), 6.41 (d, J = 2.0 Hz, 1H), 3.79 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), major isomer, δ 161.8, 149.2, 149.0, 133.7, 132.8, 131.8, 130.9, 130.3, 127.1, 123.5, 121.1, 111.5, 111.4, 93.1, 56.1, 56.0, 49.7 (the ^{13}C NMR data of the minor isomer was not collected because of the low concentration); HRMS (ESI) m/z calcd for $C_{17}H_{15}{}^{35}ClNO_3^+$ $[M + H]^+$ 316.0735, found 316.0739.

3-(4-Chlorophenyl)-2-(3,4-dimethoxyphenyl)-3-oxopropanenitrile (1g). **1g** was purified by silica gel chromatography (EA/PE = 25/75): yield 2.970 g, 72%, white solid, mp 105−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 6.95 (dd, J = 8.0, 2.0 Hz, 1H), 6.88−6.85 (m, 2H), 5.50 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 149.9, 149.8, 141.0, 132.0, 130.6, 129.3, 122.2, 121.0, 116.6, 111.9, 110.8, 56.1, 55.9, 46.5; HRMS (ESI) m/z calcd for $C_{17}H_{15}{}^{35}ClNO_3^+$ $[M + H]^+$ 316.0735, found 316.0739.

3-(3-Bromophenyl)-2-(3,4-dimethoxyphenyl)-3-oxopropanenitrile (1h). **1h** was purified by silica gel chromatography (EA/PE = 20/80): yield 3.160 g, 78%, white solid, mp 151−153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 6.95 (dd, J = 8.0, 2.0 Hz, 1H), 6.88 (d, J = 2.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H) 5.51 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 150.0, 149.9, 137.2, 135.4, 132.2, 130.5, 127.6, 123.3, 121.9, 121.1, 116.4, 111.9, 110.8, 56.1, 56.0, 46.5; HRMS (ESI) m/z calcd for $C_{17}H_{15}{}^{79}BrNO_3^+$ $[M + H]^+$ 360.0230, found 360.0233.

2-(3,4-Dimethoxyphenyl)-3-(4-fluorophenyl)-3-oxopropanenitrile (1i). **1i** was purified by silica gel chromatography (EA/PE = 25/75): yield 2.165 g, 64%, white solid, mp 102−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.94 (m, 2H), 7.11 (t, J = 8.5 Hz, 2H), 6.97 (dd, J = 8.0, 2.0 Hz, 1H), 6.90 (d, J = 2.0 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 5.59 (s, 1H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 166.2 (d, J_{F-C} = 256 Hz), 149.9, 149.8, 132.0 (d, J_{F-C} = 10 Hz), 130.1, 122.4, 121.0, 116.2 (d, J_{F-C} = 22 Hz), 116.1, 111.9, 110.9, 56.1, 55.9, 46.4; HRMS (ESI) m/z calcd for $C_{17}H_{15}FNO_3^+$ $[M + H]^+$ 300.1030, found 300.1030.

(*E*)-3-(3,4-Dichlorophenyl)-2-(3,4-dimethoxyphenyl)-3-hydroxyacrylonitrile (1j). **1j** was purified by silica gel chromatography (EA/PE = 20/80): yield 2.955 g, 75%, yellow solid, mp 133−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 2.0 Hz, 1H), 7.80 (dd, J = 8.0, 2.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.09 (dd, J = 8.0, 2.0 Hz, 1H), 7.00 (d, J = 2.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.55 (s, 1H), 3.92 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.0, 148.8, 148.6, 136.6, 133.5, 131.7, 131.1, 131.0, 129.9, 129.5, 125.4, 122.4, 120.9, 112.3, 112.1, 89.9, 56.0; HRMS (ESI) m/z calcd for $C_{17}H_{14}{}^{35}Cl_2NO_3^+$ $[M + H]^+$ 350.0345, found 350.0349.

2-(3,4-Dimethoxyphenyl)-3-oxo-3-(3-(trifluoromethyl)-phenyl)propanenitrile (1k). **1k** was purified by silica gel chromatography (EA/PE = 20/80): yield 2.245 g, 57%, white solid, mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.62 (t, J = 8.0 Hz, 1H), 6.99 (dd, J = 8.0, 2.0 Hz, 1H), 6.90 (d, J = 2.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 5.58 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 187.9, 150.1, 150.0, 134.2, 132.2, 131.7 (d, J_{F-C} = 33.2 Hz), 130.6 (d, J_{F-C} = 3.3 Hz), 129.7, 126.0 (q, J_{F-C} = 3.7 Hz), 123.3 (q, J_{F-C} = 271 Hz), 121.7, 121.0, 116.2, 112.0, 110.9, 56.1, 56.0, 46.8; HRMS (ESI) m/z calcd for $C_{18}H_{15}F_3NO_3^+$ $[M + H]^+$ 350.0999, found 350.1003.

2-(3,4-Dimethoxyphenyl)-3-oxo-3-(4-(trifluoromethyl)-phenyl)propanenitrile (1l). **1l** was purified by silica gel chromatography (EA/PE = 20/80): yield 2.640 g, 67%, white solid, mp 91−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.12 (dd, J = 8.0, 2.0 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.56 (s, 1H), 3.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 150.0 (d, J_{F-C} = 10.3 Hz), 136.4, 135.4 (q, J_{F-C} = 32.8 Hz), 129. 6, 128.7, 126.0 (q, J_{F-C} = 3.7 Hz), 123.2 (q, J_{F-C} = 271 Hz), 121.7, 121.1, 116.4, 110.8, 56.1, 55.9, 46.8; HRMS (ESI) m/z calcd for $C_{18}H_{15}F_3NO_3^+$ $[M + H]^+$ 350.0999, found 350.1003.

2-(3,4-Dimethoxyphenyl)-3-oxo-3-(pyridin-4-yl)-propanenitrile (1m). **1m** was purified by silica gel chromatography (EA/PE = 20/80): yield 1.910 g, 60%, yellow solid, mp 221−223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 6.0 Hz, 1H), 8.48 (d, J = 6.0 Hz, 1H), 7.76 (d, J = 6.0 Hz, 1H), 7.71−7.65 (m, 1H), 7.31 (d, J = 8.0 Hz, 1H), 6.95 (dd, J = 8.0, 2.0 Hz, 1H), 6.86 (d, J = 8.0, 1H), 5.45 (s, 1H), 3.92 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.3, 150.2, 148.8, 148.5, 143.8, 125.3, 123.8, 123.4, 120.8, 112.2, 111.8, 89.7, 56.0, 55.9; HRMS (ESI) m/z calcd for $C_{16}H_{15}N_2O_3^+$ $[M + H]^+$ 283.1077, found 283.1078.

2-(3,4-Dimethoxyphenyl)-3-(furan-2-yl)-3-oxopropanenitrile (1o). **1o** was purified by silica gel chromatography (EA/PE = 15/85): yield 1.745 g, 57%, white solid, mp 98−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.36 (d, J = 3.5 Hz, 1H), 7.02 (dd, J = 8.0, 2.0 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.65−6.49 (m, 1H), 5.41 (s, 1H), 3.88 (s, 3H), 3.86 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 149.8, 149.7, 147.8, 122.1, 121.2, 120.4, 116.4, 113.4, 111.7, 111.1, 56.1, 55.9, 46.0 (one carbon peak was missing because of overlapping); HRMS (ESI) m/z calcd for $C_{15}H_{14}NO_4^+$ $[M + H]^+$ 272.0917, found 272.0919.

(*E*)-2-(3,4-Dimethoxyphenyl)-3-oxo-5-phenylpent-4-enenitrile (1p). **1p** was purified by silica gel chromatography (EA/PE = 20/80): yield 2.080 g, 60%, yellow solid, mp 149−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.0 Hz, 2H), 7.45−7.37 (m, 3H), 7.35 (d, J = 6.0 Hz, 1H), 7.18 (d, J = 16.0 Hz, 1H), 7.05 (dd, J = 8.0, 2.0 Hz, 1H), 6.98 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.28 (s, 1H), 3.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 161.0, 146.9, 136.6, 131.5, 129.1, 127.7, 123.2, 120.3, 119.0, 116.6, 112.0, 111.6, 110.7, 56.1, 56.0, 49.7; HRMS (ESI) m/z calcd for $C_{19}H_{18}NO_3^+$ $[M + H]^+$ 308.1281, found 308.1281.

2-(7-Methoxynaphthalen-1-yl)-3-oxo-3-phenylpropanenitrile (1u). **1u** was purified by silica gel chromatography (EA/PE = 15/85): yield 0.855 g, 55%, white solid, mp 131−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.58 (d, J = 7.0 Hz, 1H), 7.52 (t, J = 7.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 2H), 7.32 (d, J = 7.5 Hz, 1H), 7.30−7.26 (m, 1H), 7.20 (dd, J = 9.0, 2.0 Hz, 1H), 6.13 (s, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 159.0, 134.3, 134.1, 131.7, 130.9, 129.9, 129.7, 129.1, 129.0, 128.6, 125.2, 123.3, 119.1, 116.2, 101.5, 55.5, 45.3; HRMS (ESI) m/z calcd for $C_{20}H_{16}NO_2^+$ $[M + H]^+$ 302.1176, found 302.1178.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-phenyl-1*H*-indene-1,3-dicarbonitrile (2a). **2a** was purified by silica gel chromatography (EA/PE = 15/85): yield 0.077 g, 88%, yellow green solid, mp 163−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.14 (s, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.84−6.80 (m, 2H), 6.62 (s, 1H), 4.02 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 151.3, 151.0, 150.2, 149.9, 137.4, 131.1, 130.8, 129.4, 128.3, 126.2, 118.9, 118.5, 115.1, 113.2, 112.1, 108.8, 108.8, 107.3, 104.2, 57.5, 56.8, 56.8,

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56.4, 56.3; HRMS (ESI) m/z calcd for $C_{27}H_{26}N_3O_4^+$ $[M + NH_4]^+$ 456.1918, found 456.1917.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-*o*-tolyl-1*H*-indene-1,3-dicarbonitrile (2b). **2b** was purified by silica gel chromatography (EA/PE = 15/85): yield 0.063 g, 69%, white solid, mp 184−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.14 (s, 2H), 7.02 (s, 2H), 6.73 (d, J = 8.0 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 6.41 (s, 1H), 4.03 (s, 3H), 3.91 (s, 3H), 3.86 (s, 3H), 3.59 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 151.1, 150.5, 149.9, 149.3, 137.6, 134.7, 131.4, 130.6, 129.9, 129.8, 128.7, 125.5, 124.3, 119.2, 117.7, 116.0, 113.5, 111.2, 110.3, 107.9, 104.0, 59.0, 56.5, 56.5, 55.9, 55.8, 19.2; HRMS (ESI) m/z calcd for $C_{28}H_{28}N_3O_4^+$ $[M + NH_4]^+$ 470.2074, found 470.2070.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-(2-methoxyphenyl)-1*H*-indene-1,3-dicarbonitrile (2c). **2c** was purified by silica gel chromatography (EA/PE = 15/85): yield 0.086 g, 92%, yellow green solid, mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.14 (s, 1H), 6.94 (d, J = 8.5 Hz, 2H), 6.91−6.86 (m, 2H), 6.77 (d, J = 8.5 Hz, 1H), 6.51 (s, 1H), 4.01 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 153.5, 151.1, 150.6, 149.7, 149.6, 136.7, 131.9, 131.5, 129.5, 125.6, 120.7, 120.2, 119.2, 118.3, 117.2, 114.2, 111.7, 111.5, 109.3, 107.6, 104.1, 58.6, 56.6, 56.1, 55.4 (two OMe carbon peaks were missing because of overlapping); HRMS (ESI) m/z calcd for $C_{28}H_{28}N_3O_5^+$ $[M + NH_4]^+$ 486.2023, found 486.2020.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-(3-methoxyphenyl)-1*H*-indene-1,3-dicarbonitrile (2d). **2d** was purified by silica gel chromatography (EA/PE = 20/80): yield 0.084 g, 90%, yellow green solid, mp 170−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.28 (m, 3H), 7.14 (s, 1H), 7.00 (d, J = 9.5 Hz, 1H), 6.95 (d, J = 5.5 Hz, 1H), 6.84 (d, J = 9.0 Hz, 2H), 6.62 (s, 1H), 4.02 (s, 3H), 3.87 (s, 6H), 3.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 155.8, 151.0, 150.8, 149.9, 149.7, 137.1, 131.6, 130.7, 130.0, 126.0, 120.4, 118.5, 118.1, 117.0, 114.7, 113.0, 112.9, 111.9, 108.7, 107.0, 103.9, 57.2, 56.4, 56.1, 55.9, 55.4 (one carbon peak was missing because of overlapping); HRMS (ESI) m/z calcd for $C_{28}H_{28}N_3O_5^+$ $[M + NH_4]^+$ 486.2023, found 486.2020.

2-(2,3-Dimethoxyphenyl)-1-(3,4-dimethoxyphenyl)-5,6-dimethoxy-1*H*-indene-1,3-dicarbonitrile (2e). **2e** was purified by silica gel chromatography (EA/PE = 20/80): yield 0.080 g, 80%, yellow green solid, mp 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.03−6.91 (m, 3H), 6.82−6.72 (m, 3H), 6.58 (s, 1H), 4.03 (s, 3H), 3.90 (s, 3H), 3.86 (s, 6H), 3.70 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 153.3, 151.5, 151.0, 150.1, 149.9, 148.2, 136.6, 132.0, 125.6, 125.3, 123.9, 121.4, 119.6, 118.6, 117.5, 115.2, 114.3, 111.8, 110.3, 108.0, 104.5, 61.6, 59.0, 56.9, 56.9, 56.4, 56.4, 56.3; HRMS (ESI) m/z calcd for $C_{29}H_{30}N_3O_6^+$ $[M + NH_4]^+$ 516.2129, found 516.2126.

2-(2-Chlorophenyl)-1-(3,4-dimethoxyphenyl)-5,6-dimethoxy-1*H*-indene-1,3-dicarbonitrile (2f). **2f** was purified by silica gel chromatography (EA/PE = 15/85): yield 0.065 g, 69%, yellow green solid, mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.28−7.20 (m, 2H), 7.18 (s, 1H), 6.98 (s, 1H), 6.81−6.71 (m, 2H), 6.46 (s, 1H), 4.05 (s, 3H), 3.91 (s, 3H), 3.87 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 151.1, 150.9, 149.9, 149.4, 135.6, 134.3, 131.2, 131.0, 130.3, 130.0, 129.5, 126.6, 123.7, 119.5, 118.2, 117.4, 113.2, 111.3, 109.8, 107.6, 104.2, 58.8, 56.5, 55.9, 55.9 (one OMe carbon peak was missing because of overlapping); HRMS (ESI) m/z calcd for $C_{27}H_{25}{}^{35}ClN_3O_4^+$ $[M + NH_4]^+$ 490.1528, found 490.1526.

2-(4-Chlorophenyl)-1-(3,4-dimethoxyphenyl)-5,6-dimethoxy-1*H*-indene-1,3-dicarbonitrile (2g). **2g** was purified by silica gel chromatography (EA/PE = 20/80): yield 0.081 g, 86%, yellow green solid, mp 121−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.29 (s, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 2H), 6.59 (s, 1H), 4.02 (s, 3H), 3.88 (s, 6H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 151.5, 151.4, 150.4, 150.2, 137.5, 137.3, 130.9, 129.9, 129.6, 129.3, 125.9, 119.0, 118.4, 115.0, 113.7, 112.3, 108.8, 107.4, 104.3, 57.6, 56.9, 56.9, 56.6, 56.4; HRMS (ESI) m/z calcd for $C_{27}H_{25}{}^{35}ClN_3O_4^+$ $[M + NH_4]^+$ 490.1528, found 490.1526.

2-(3-Bromophenyl)-1-(3,4-dimethoxyphenyl)-5,6-dimethoxy-1*H*-indene-1,3-dicarbonitrile (2h). **2h** was purified by silica gel chromatography (EA/PE = 15/85): yield 0.094 g, 91%, yellow green solid, mp 189−191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.13 (s, 1H), 6.92 (dd, J = 8.0, 2.0 Hz, 1H), 6.88−6.76 (m, 2H), 6.59 (d, J = 2.0 Hz, 1H), 4.01 (s, 3H), 3.87 (s, 6H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 151.6, 151.5, 150.4, 150.3, 137.6, 134.0, 132.9, 131.1, 131.0, 130.9, 127.0, 125.6, 123.6, 119.1, 118.2, 114.6, 114.6, 112.4, 109.1, 107.4, 104.4, 57.7, 57.0, 56.9, 56.6, 56.4; HRMS (ESI) m/z calcd for $C_{27}H_{25}{}^{79}BrN_3O_4^+$ $[M + NH_4]^+$ 534.1023, found 534.1023.

1-(3,4-Dimethoxyphenyl)-2-(4-fluorophenyl)-5,6-dimethoxy-1*H*-indene-1,3-dicarbonitrile (2i). **2i** was purified by silica gel chromatography (EA/PE = 20/80): yield 0.061 g, 67%, yellow green solid, mp 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.67 (m, 2H), 7.13 (s, 1H), 7.08 (t, J = 8.5 Hz, 2H), 6.98 (dd, J = 8.5, 2.0 Hz, 1H), 6.84 (d, J = 7.5 Hz, 2H), 6.59 (d, J = 2.0 Hz, 1H), 4.01 (s, 3H), 3.87 (s, 6H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, J_{F-C} = 252 Hz), 154.7, 151.0, 150.8, 149.9, 149.7, 136.87, 130.6, 130.1 (d, J_{F-C} = 8.4 Hz), 126.7 (d, J_{F-C} = 3.3 Hz), 125.6, 118.5, 117.9, 116.3 (d, J_{F-C} = 21.8 Hz), 114.6, 112.9, 111.9, 108.4, 107.0, 103.9, 57.3, 56.4, 56.4, 56.1, 55.9; HRMS (ESI) m/z calcd for $C_{27}H_{25}FN_3O_4^+$ $[M + NH_4]^+$ 474.1824, found 474.1823.

2-(3,4-Dichlorophenyl)-1-(3,4-dimethoxyphenyl)-5,6-dimethoxy-1*H*-indene-1,3-dicarbonitrile (2j). **2j** was purified by silica gel chromatography (EA/PE = 20/80): yield 0.083 g, 82%, yellow green solid, mp 153−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 2.0 Hz, 1H), 7.53 (dd, J = 8.5, 2.0 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.12 (s, 1H), 6.93 (dd, J = 8.5, 2.0 Hz, 1H), 6.83 (t, J = 5.0 Hz, 2H), 6.57 (d, J = 2.0 Hz, 1H), 4.00 (s, 3H), 3.87 (s, 6H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 152.9, 151.2, 151.1, 150.0, 149.9, 137.2, 135.0, 133.5, 131.1, 130.2, 129.4, 127.0, 124.9, 118.5, 117.6, 114.3, 114.1, 111.9, 108.3, 106.8, 103.9, 57.1, 56.5, 56.4, 56.1, 55.9; HRMS (ESI) m/z calcd for $C_{27}H_{24}{}^{35}Cl_2N_3O_4^+$ $[M + NH_4]^+$ 524.1138, found 524.1135.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-(3-(trifluoromethyl)phenyl)-1*H*-indene-1,3-dicarbonitrile (2k). **2k** was purified by silica gel chromatography (EA/PE = 25/75): yield 0.085 g, 84%, yellow green solid, mp 219−221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.14 (s, 1H), 6.92 (dd, J = 8.0, 2.0 Hz, 1H), 6.86 (s, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 2.0 Hz, 1H), 4.01 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 151.2, 151.2, 150.0 (d, J_{F-C} = 9.7 Hz), 137.2, 131.9, 131.8 (q, J_{F-C} = 32.7 Hz), 131.2, 131.1, 130.4, 129.7, 127.0, 124.9, 124.5 (q, J_{F-C} = 3.6 Hz), 123.5 (q, J_{F-C} = 271 Hz), 118.6, 117.6, 114.5, 114.1, 112.0, 108.6, 107.0, 104.0, 57.3, 56.4, 56.4, 56.1, 55.9; HRMS (ESI) m/z calcd for $C_{28}H_{25}F_3N_3O_4^+$ $[M + NH_4]^+$ 524.1792, found 524.1790.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-(4-(trifluoromethyl)phenyl)-1*H*-indene-1,3-dicarbonitrile (2l). **2l** was purified by silica gel chromatography (EA/PE = 20/80): yield 0.082 g, 81%, yellow green solid, mp 219−221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.15 (s, 1H), 6.93 (dd, J = 8.0, 2.0 Hz, 1H), 6.88−6.80 (m, 2H), 6.60 (d, J = 2.0 Hz, 1H), 4.02 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ153.9, 151.3, 151.2, 150.0, 149.9, 137.3, 133.8, 132.0 (q, J_{F-C} = 32.7 Hz), 130.3, 128.2, 126.0 (q, J_{F-C} = 3.7 Hz), 125.0, 123.5 (q, J_{F-C} = 271 Hz), 118.6, 117.7, 114.9, 114.1, 111.9, 108.4, 106.9, 104.1, 57.3, 56.5, 56.4, 56.1, 55.9; HRMS (ESI) m/z calcd for $C_{28}H_{25}F_3N_3O_4^+$ $[M + NH_4]^+$ 524.1792, found 524.1790.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-(pyridin-4-yl)-1*H*-indene-1,3-dicarbonitrile (2m). **2m** was purified by silica gel chromatography (EA/PE = 20/80): yield 0.072 g, 82%, yellow green solid, mp 205−207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 5.0 Hz, 2H), 7.58 (d, J = 5.0 Hz, 2H), 7.16 (s, 1H), 6.97 (d, J = 7.0 Hz,

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1H), 6.90−6.80 (m, 2H), 6.58 (s, 1H), 4.01 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H) 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 151.6, 151.2, 150.7, 150.0, 149.9, 137.7, 137.3, 130.0, 124.7, 121.2, 118.5, 117.5, 116.1, 113.8, 112.0, 108.2, 106.8, 104.1, 56.8, 56.5, 56.4, 56.1, 55.9; HRMS (ESI) m/z calcd for $C_{26}H_{22}N_3O_4^+$ $[M + NH_4]^+$ 440.1605, found 440.1606.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-(thiophen-2-yl)-1*H*-indene-1,3-dicarbonitrile (2n). **2n** was purified by silica gel chromatography (EA/PE = 20/80): yield 0.072 g, 81%, yellow green solid, mp 191−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 3.0 Hz, 1H), 7.48 (d, J = 5.0 Hz, 1H), 7.13−7.02 (m, 3H), 6.88 (d, J = 8.0 Hz, 1H), 6.80 (s, 1H), 6.67 (s, 1H), 4.00 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 150.5, 149.9, 149.8, 149.7, 136.5, 133.2, 130.6, 130.3, 129.9, 128.0, 126.1, 118.8, 118.0, 114.8, 111.8, 109.1, 108.6, 106.9, 103.7, 57.3, 56.4, 56.4, 56.1, 55.9; HRMS (ESI) m/z calcd for $C_{25}H_{21}N_2O_4S$ $[M + NH_4]^+$ 445.1217, found 445.1219.

1-(3,4-Dimethoxyphenyl)-2-(furan-2-yl)-5,6-dimethoxy-1*H*-indene-1,3-dicarbonitrile (2o). **2o** was purified by silica gel chromatography (EA/PE = 25/85): yield 0.061 g, 71%, yellow green solid, mp 204−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.09 (s, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.91−6.72 (m, 3H), 6.64 (s, 1H), 6.47 (s, 1H), 3.98 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H) 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 150.5, 149.7, 149.7, 146.5, 145.4, 144.5, 136.2, 130.7, 126.4, 118.4, 117.8, 114.5, 114.4, 112.7, 111.7, 108.5, 107.7, 107.1, 103.8, 56.4, 56.1, 55.9, 55.4 (one OMe carbon peak was missing because of overlapping); HRMS (ESI) m/z calcd for $C_{25}H_{21}N_2O_5^+$ $[M + NH_4]^+$ 429.1445, found 429.1448.

(*E*)-1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-styryl-1*H*-indene-1,3-dicarbonitrile (2p). **2p** was purified by silica gel chromatography (EA/PE = 15/75): yield 0.060 g, 65%, yellow green solid, mp 230−232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.0 Hz, 2H), 7.40−7.30 (m, 3H), 7.21 (d, J = 16.0 Hz, 1H), 7.14−7.05 (m, 2H), 7.00 (d, J = 16.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.82 (s, 1H), 6.64 (s, 1H), 4.00 (s, 3H), 3.90 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 151.5, 151.3, 150.5, 150.2, 138.3, 137.9, 135.9, 130.8, 130.2, 129.4, 128.0, 127.2, 118.8, 118.6, 1178.0, 114.4, 113.9, 112.4, 108.8, 107.5, 104.2, 56.9, 56.7, 56.4, 55.4 (one OMe carbon peak was missing because of overlapping); HRMS (ESI) m/z calcd for $C_{29}H_{28}N_3O_4^+$ $[M + NH_4]^+$ 482.2074, found 482.2071.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-methyl-1*H*-indene-1,3-dicarbonitrile (2q). **2q** was purified by silica gel chromatography (EA/PE = 10/90): yield 0.051 g, 68%, white solid, mp 175−177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.88−6.78 (m, 3H), 6.50 (s, 1H), 3.98 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 150.8, 150.0, 149.8, 135.6, 131.0, 125.0, 118.8, 117.3, 114.1, 113.5, 111.7, 108.6, 107.5, 103.5, 58.0, 56.4, 56.3, 56.1, 56.0, 13.4 (one OMe carbon peak was missing because of overlapping); HRMS (ESI) m/z calcd for $C_{22}H_{24}N_3O_4^+$ $[M + NH_4]^+$ 394.1761, found 394.1760.

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-propyl-1*H*-indene-1,3-dicarbonitrile (2r). **2r** was purified by silica gel chromatography (EA/PE = 10/90): yield 0.063 g, 78%, yellow solid, mp 131−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.95−6.76 (m, 3H), 6.48 (s, 1H), 3.98 (s, 3H), 3.89 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 2.57−2.40 (m, 2H), 1.65−1.59 (m, 2H), 0.94 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 150.8, 150.0, 149.8, 149.7, 135.8, 131.1, 124.9, 119.0, 117.6, 114.2, 113.8, 111.6, 108.6, 107.3, 103.4, 57.7, 56.4, 56.4, 56.1, 56.0, 30.8, 21.8, 14.1; HRMS (ESI) m/z calcd for $C_{24}H_{28}N_3O_4^+$ $[M + NH_4]^+$ 422.2074, found 422.2071.

6-Methoxy-1-(4-methoxyphenyl)-2-phenyl-1*H*-indene-1,3-dicarbonitrile (2s). **2s** was purified by silica gel chromatography (EA/PE = 15/75): yield 0.042 g, 55%, white solid, mp 134−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.70 (m, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.43−7.31 (m, 3H), 7.22 (d, J = 8.5 Hz, 2H), 7.01 (dd, J = 8.5, 2.0 Hz, 1H), 6.85 (m, 3H), 3.80 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 160.0, 154.8, 146.5, 130.7, 130.7, 130.4, 129.0, 128.0, 127.0, 125.7, 122.2, 118.0, 115.5, 115.1, 114.6, 112.6, 110.2, 56.9, 55.8, 55.3; HRMS (ESI) m/z calcd for $C_{25}H_{22}N_3O_2^+$ $[M + NH_4]^+$ 396.1707, found 396.1703.

5-Methoxy-1-(3-methoxyphenyl)-2-methyl-1*H*-indene-1,3-dicarbonitrile (2t). **2t** was purified by silica gel chromatography (EA/PE = 15/75): yield 0.037 g, 58%, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.92−6.82 (m, 2H), 6.77 (d, J = 8.0 Hz, 1H), 6.70 (s, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 161.1, 160.4, 139.9, 135.1, 134.6, 130.7, 125.2, 118.0, 117.0, 115.0, 114.6, 114.0, 113.1, 112.2, 106.1, 57.7, 55.8, 55.4, 13.6; HRMS (ESI) m/z calcd for $C_{20}H_{20}N_3O_2^+$ $[M + NH_4]^+$ 334.1550, found 334.1550.

8-Methoxy-3-(7-methoxynaphthalen-1-yl)-2-phenyl-3*H*-cyclopenta[*a*]naphthalene-1,3-dicarbonitrile (2u). **2u** was purified by silica gel chromatography (EA/PE = 20/80): yield 0.072 g, 75%, yellow green solid, mp 205−207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.43 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.64 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 8.0 Hz, 1H), 7.42−7.29 (m, 4H), 7.20 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 9.0 Hz, 1H), 6.27 (s, 1H), 4.09 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 159.7, 158.3, 143.0, 132.0, 131.0, 130.8, 130.7, 130.6, 130.5, 129.8, 129.7, 129.5, 129.2, 129.0, 128.2, 126.1, 123.2, 120.4, 119.2, 118.3, 117.6, 117.1, 112.7, 101.0, 100.8, 60.6, 55.7, 54.7 (two carbon were missing because of overlapping); HRMS (ESI) m/z calcd for $C_{33}H_{26}N_3O_2^+$ $[M + NH_4]^+$ 496.2020, found 496.2018.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data for all new compounds and X-ray structural data of **2a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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